105. The Synthesis and Reactions of 1-(2-Propynyl)pyridinium Salts

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Summary

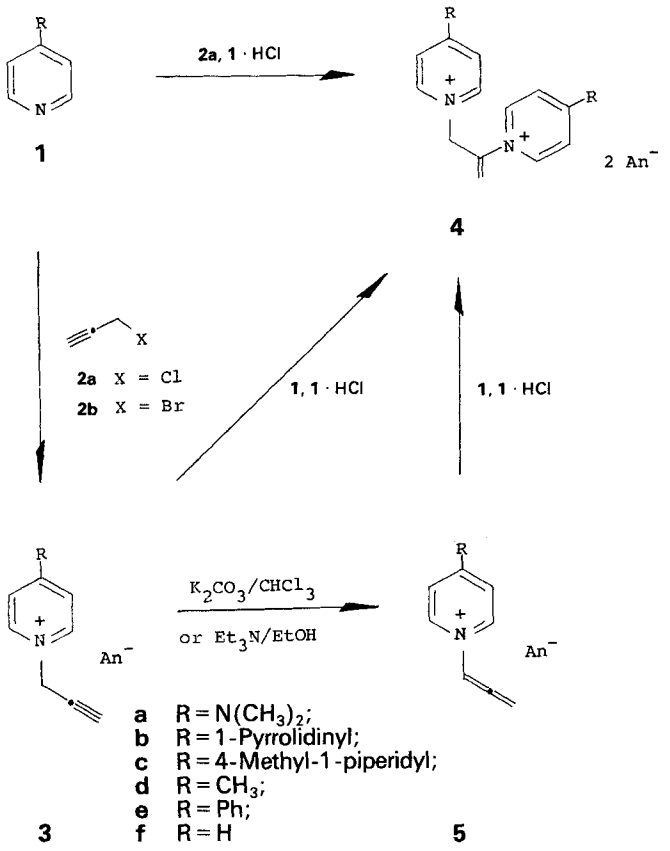
The synthesis of 1-(2-propynyl)pyridinium salts **3** is described. Compounds **3** react with a second pyridine molecule, in the presence of the corresponding hydrochloride, to form products of type **4**. Certain bases cause the 1-(2-propynyl)pyridinium salts **3** to rearrange into 1-propadienylpyridinium salts **5**. Diethylamine converts compounds **3** into 1-acetonylpyridinium salts **8**. Moreover, treatment of **3** or **5** with sodium methoxide gives enol ethers of type **9**, which can be hydrolyzed to the ketones **8**. Addition of bromine to some of the unsaturated compounds is also reported.

The chemistry of 1-vinyl- and 1-allyl-pyridinium salts has recently received more attention [1], but little is known about the 1-(1-propynyl) and 1-(2-propynyl) analogues. Reportedly, treatment of pyridine with 2-propynyl halides at 0 °C for 18 h gave the 1-(2-propynyl)pyridinium halide **3f** [2], while heating both reagents in a sealed tube for 15 h at 70 °C [3] or 30 h at 60 °C [4] afforded polymers of 1-(2-propenyl)pyridinium salts.

We have examined the reactions of several pyridines with these halides and found a significant influence of the 4-substituent on the course of the reaction. Pyridines with a strong electron-donor substituent in the 4-position **1a–c** gave with 2-propynyl halides **2a** or **2b** the expected 1-(2-propynyl)pyridinium salts (**3a–c**) in high yields. γ-Picoline (**1d**) and 4-phenylpyridine (**1e**), however, are much less reactive and gave **3d** and **3e** only in moderate yields. The ^{1}H-NMR spectra of compounds **3a–e** are characterized by a triplet near 2.8 ppm (in **3d** at 2.95 ppm) and a doublet in the region 4.5–5.4 ppm due to the propynyl substituent. The coupling constants of 3 Hz agree with the expected value for a ^4J coupling. The ^{13}C-NMR spectra confirm structures **3** *(Table 1)*.

Extending the reaction time between **1d** and **2b** to 12 h improved the yield of **3d**. However, 4-phenylpyridine (**1e**) behaved differently. Nucleophilic attack of a second mole of 4-phenylpyridine (**1e**) converted initially formed **3e** into the pyridinium halide **4e**. Compound **4e** was also obtained in high yield by refluxing **1e** with 2-propynyl bromide (**2b**) in EtOH for 30 min. Treatment of pyridine **1f** with the 2-propynyl halides **2a** or **2b** for 18 h either at 0 °C or at 70 °C gave a mixture shown spectroscopically to

Schema 1



contain **4f** rather than **3f**. Moreover, when **2a** reacted with pyridine in the presence of pyridine hydrochloride, pure **4f** was formed. Product **4d** was also obtained directly from **1d** and **1d** · HCl, with **2a**. However, preparation of **4a** and **4b** was only accomplished by treatment of **3a** and **3b** with the corresponding pyridine in the presence of equimolar amounts of **1a** · HCl and **1b** · HCl, respectively, which suppressed the formation of intractable polymeric by-products.

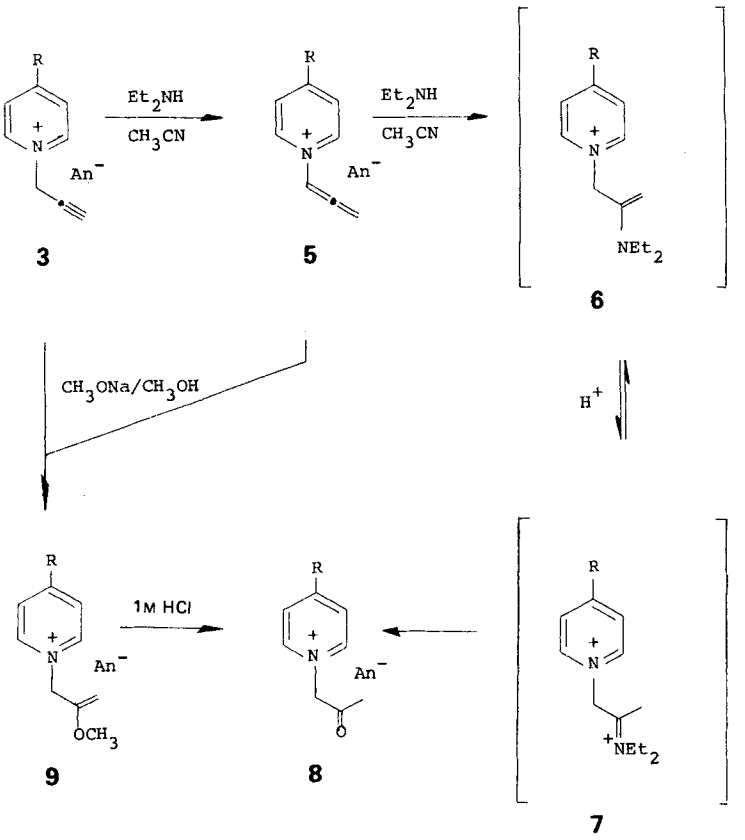
The structure assignment of compounds **4** is based on spectral evidence. In the ^{1}H-NMR spectrum the olefinic methylene protons appear as an *AB*-system in the region 5.7–6.2 ppm, while the *N*-methylene protons appear as a singlet (5.4–6.2 ppm). No allylic coupling is observed. Increasing the electron-donor character of the 4-substituent causes a diamagnetic shift of the A_2X_2-system of the pyridine protons. The ^{13}C-NMR spectra display a triplet and a singlet corresponding to the olefinic C-atoms and a triplet for the saturated methylene C-atom, thus confirming the structure of the C_3-moiety. The α-, β-, and γ-C-atom of the two pyridine rings are nonequivalent and therefore give rise to six signals *(Table 1)*.

Table 1. *^{13}C-NMR Spectra*[a]) *of Compounds Reported*

Comp.	Anion	N(1) Substituent			Pyridinium ring			Pyridine-4-substituent
		C(1)	C(2)	C(3)	α-C	β-C	γ-C	
3a[b])	ClO_4^-	45.7 (*t*)	77.0 (*s*)	79.1 (*d*)	141.4 (*d*)	107.9 (*d*)	156.0 (*s*)	39.8 (*q*, $N(CH_3)_2$)
3b	ClO_4^-	46.8 (*t*)	73.6 (*s*)	78.4 (*d*)	140.7 (*d*)	108.8 (*d*)	154.2 (*s*)	48.9 (*t*, CH_2NCH_2); 24.9 (*t*, CH_2CH_2)
3c	ClO_4^-	46.9 (*t*)	73.3 (*s*)	78.7 (*d*)	141.4 (*d*)	108.5 (*d*)	155.9 (*s*)	47.9 (*t*, CH_2NCH_2); 33.5 (*t*, CH_2CH_2); 30.68 (*d*, CH–); 20.5 (*q*, CH_3)
3d	Br^-	50.2 (*t*)	72.0 (*s*)	80.6 (*d*)	142.6 (*d*)	129.2 (*d*)	161.7 (*s*)	21.5 (*t*, CH_3)
3e	ClO_4^-	50.2 (*t*)	72.2 (*s*)	80.1 (*d*)	143.5 (*d*)	133.5 (*d*)	159.4 (*s*)	133.4 (*s*, C(1)); 130.3 (*d*, C(2)); 125.5 (*d*, C(3)); 128.5 (*d*, C(4))
4a[b])	ClO_4^-	57.0 (*t*)	142.7 (*s*)	117.9 (*t*)	141.8 (*d*)	108.1 (*d*)	156.2 (*s*)	40.1 (*q*, $-N(CH_3)_2$)
					140.2 (*d*)	107.7 (*d*)	156.1 (*s*)	39.8 (*q*, $-N(CH_3)_2$)
4b	ClO_4^-	58.5 (*t*)	142.9 (*s*)	119.4 (*t*)	141.4 (*d*)	109.2 (*d*)	154.5 (*s*)	49.3 (*t*, CH_2NCH_2);
					139.9 (*d*)	109.2 (*d*)	154.3 (*s*)	49.1 (*t*, CH_2NCH_2); 24.8 (*t*, CH_2CH_2)
4d	ClO_4^-	61.2 (*t*)	142.2 (*s*)	123.6 (*t*)	144.2 (*d*)	130.1 (*d*)	164.3 (*s*)	21.9 (*q*, CH_3)
					142.8 (*d*)	129.8 (*d*)	163.5 (*s*)	21.8 (*q*, CH_3)
4e	Br^-	60.2 (*t*)	141.9 (*s*)	122.4 (*t*)	145.7 (*d*)	125.5 (*d*)	159.3 (*s*)	133.4 (*d*); 133.3 (*d*); 132.8 (*s*);
					144.2 (*d*)	125.3 (*d*)	158.8 (*s*)	130.0 (*d*); 128.1 (*d*)
4f	ClO_4^-	62.3 (*t*)	142.8 (*s*)	124.2 (*t*)	145.5 (*d*)	130.0 (*d*)	148.8 (*d*)	
					144.4 (*d*)	129.7 (*d*)	148.3 (*d*)	
5a[b])	ClO_4^-	103.3 (*d*)	200.7 (*s*)	92.5 (*t*)	138.5 (*d*)	108.1 (*d*)	155.9 (*s*)	39.9 (*q*, $N(CH_3)_2$)
5b	ClO_4^-	103.5 (*d*)	201.6 (*s*)	92.1 (*t*)	138.3 (*d*)	108.7 (*d*)	153.8 (*s*)	48.9 (*t*, CH_2NCH_2); 24.8 (*t*, CH_2CH_2)
5c	Br^-	103.2 (*d*)	201.6 (*s*)	92.0 (*t*)	138.7 (*d*)	108.2 (*d*)	155.3 (*s*)	47.7 (*t*, CH_2NCH_2); 33.3 (*t*, CH_2CH_2); 30.3 (*d*, CH); 20.5 (*q*, CH_3)
5d	ClO_4^-	105.1 (*d*)	202.9 (*s*)	93.4 (*t*)	140.1 (*d*)	129.2 (*d*)	161.1 (*s*)	21.6 (*q*, CH_3)
5e	ClO_4^-	105.8 (*d*)	203.2 (*s*)	93.7 (*t*)	140.9 (*d*)	133.5 (*d*)	158.7 (*s*)	133.1 (*s*, C(1)); 130.3 (*d*, C(2)); 128.1 (*d*, C(3)); 125.4 (*d*, C(4))
8a	ClO_4^-	65.0 (*t*)	205.5 (*s*)	26.3 (*q*)	142.6 (*d*)	107.6 (*d*)	156.8 (*s*)	39.7 (*q*, $N(CH_3)_2$)
8b	ClO_4^-	64.9 (*t*)	205.8 (*s*)	26.1 (*q*)	142.3 (*d*)	108.2 (*d*)	154.0 (*s*)	48.6 (*t*, CH_2NCH_2); 24.4 (*t*, CH_2CH_2)
8c	ClO_4^-	64.9 (*t*)	205.6 (*s*)	26.4 (*q*)	143.0 (*d*)	107.9 (*d*)	155.6 (*s*)	47.7 (*t*, CH_2NCH_2); 33.4 (*t*, CH_2C); 30.5 (*d*, CH); 20.5 (*q*, CH_3)

[a]) In $CDCl_3/CF_3COOH$ referenced to $CDCl_3$ (77.0 ppm) except where otherwise stated; chemical shift (δ) in ppm.
[b]) In (D_6)DMSO referenced to (D_6)DMSO (39.5 ppm).

Schema 2[a])



[a]) For designation of R see *Scheme 1*.

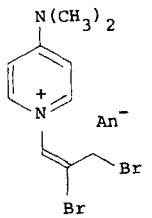
On exposure to bases, *e.g.* K_2CO_3 or Et_3N, the 1-(2-propynyl)pyridinium salts **3a–e** rearranged to 1-propadienylpyridinium salts **5a–e**. The rearrangement was indicated by the ^{1}H-NMR spectra, which exhibit a triplet in the region 7.0–7.5 ppm and a doublet near 6 ppm with characteristic allenic coupling (^4J = 6 Hz). The ^{13}C-NMR spectra confirm this structure with a signal which is characteristic for sp-allenic C-atoms *(cf. Table 5)*. This type of *N*-(2-propynyl) to *N*-allenyl rearrangement has been reported previously for *neutral* heterocyclic systems as acridones [5], carbazoles [6], and pyrazoles [7]. The only cationic example is a proposed intermediate in the benzimidazole series [8]. Presumably, these allenyl salts **5** are intermediates in the conversion of **1** or **3**, respectively, to **4**, because **5a** and **5b** have also been successfully transformed into the corresponding bis-pyridiniopropene salts **4a** and **4b**. Various attempts to induce further isomerization of **5** to give 1-(1-propynyl)pyridinium salts failed: decomposition occurred on contact with stronger bases (*e.g.* KOH).

Treatment of **5a–c** with Et_2NH in refluxing EtOH or CH_3CN led to the formation of 1-acetonylpyridinium salts **8a–c**, which were also obtained from the corresponding

1-(2-propynyl)pyridinium salts **3** without isolation of the allenic intermediate. The ^{1}H-NMR spectra contain two singlets at about 5.2 and 2.4 ppm representing the H-atoms contained in the acetonyl group. The ^{13}C-NMR spectra are also consistent with the suggested structure **8** *(Table 1)*. The reaction of **5a–c** with Et_2NH leads *via* **6** to the iminium salts **7**, which are subsequently hydrolyzed to the ketones **8**. The high yields in the sequence **1**→**3**→**8** provide a new, efficient access to these ketones, avoiding the use of lachrymatory α-halo ketones.

Treatment of **3a** and **3b** with CH_3ONa/CH_3OH at room temperature led to the 1-(2-methoxy-2-propenyl)pyridinium salts **9a** and **9b**, respectively. Since the reaction of **5a** and **5b** under similar conditions also furnished the enol ethers **9a** and **9b**, respectively; it is likely that the 1-(2-propynyl)pyridinium cations rearrange into the corresponding allenes prior to nucleophilic attack. The ^{13}C-NMR spectra of compounds **9** confirm the structure of the *N*-substituent. Chemical evidence for the formation of the enol ethers **9a** and **9b** was provided by their acid hydrolysis to the ketones **8a** and **8b**.

Although the 1-vinylpyridinium cation does not react with Br_2 at room temperature [9], 4-dimethylamino-1-vinylpyridinium bromide [1] gave the expected 1-(1,2-dibromoethyl)-4-(dimethylamino)pyridinium salt on warming in $CHCl_3$/EtOH solution [10]. When 1-propadienylpyridinium salt **5a** was allowed to react with Br_2, only the terminal double bond was attacked to yield (*E*)-1-(2,3-dibromo-1-propenyl)-4-(dimethylamino)pyridinium perchlorate (**10**). The structure of **10** was established by ^{13}C-NMR spectroscopy, which showed, besides a triplet at 60.7 ppm ($BrCH_2$), a doublet at 110.7 ppm and a singlet at 116.8 ppm, assigned to the olefinic C-atoms. Measurement of the Nuclear *Overhauser* Effect showed a significant enhancement of the signal of the aromatic α-protons on irradiating the aliphatic methylene protons, thus confirming the (*E*)-configuration of the double bond in **10**. Treatment of the 1-(2-propynyl)pyridinium salt **3a** with bromine furnished 1-(2,3-dibromo-2-propenyl)-4-(dimethylamino)-pyridinium salt (**11a**). A similar reaction of **3f**, leading to **11f**, has been reported previously [2].



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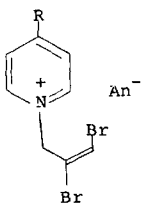

11a R = $N(CH_3)_2$

11f R = H

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Experimental Part

General. Melting points (m.p.) were determined on a hot-stage apparatus and are uncorrected. ^{1}H-NMR spectra were recorded on a *Varian EM-360L* spectrometer (60 MHz) with TMS [δ(ppm) = 0] as internal standard and ^{13}C-NMR spectra on a *JEOL-FX 100* (25 MHz) (*s* = singlet, *d* = doublet, *t* = triplet, *q* = quadruplet, *m* = multiplet). NOE measurements were done with a *Nicolet NT-300* spectrometer. The 2-propynyl bromide was used as 80% solution in toluene. Solvents were removed *in vacuo* (20 mm Hg). Anion exchange was effected by adding $NaClO_4$ (50%, 1.3 equiv.) to the bromide salt (1 equiv.) in EtOH; the perchlorate crystallized on standing at 25°.

General Procedure for the Synthesis of 4-Substituted 1-(2-Propynyl)pyridinium Salts **3**. A solution of **1** (10 mmol) in CH_2Cl_2 (5–20 ml) was added dropwise to the stirred 2-propynyl halide (10 mmol) at r.t. Stirring was continued for the time given in *Table 1*. The precipitate was filtered off and washed with Et_2O. In the case of **3a**, **b** and **e**, the hygroscopic halides were converted into the perchlorates before recrystallization *(Table 2)*.

Table 2. *Preparative and Analytical Data for 1-(2-Propynyl)pyridinium Salts* **3**

Compound	Anion	Time [h]	Yield [%]	Recrystallization solvent	M.p. [°C]	Formula	M.W.	Calc. [%] C	H	N	Found [%] C	H	N
3a	ClO_4^-	1	82[a])	EtOH	150–151	$C_{10}H_{13}ClN_2O_4$	260.7	46.07	5.02	10.75	45.89	5.15	10.6
3b	ClO_4^-	0.5	95	EtOH	127	$C_{12}H_{15}ClN_2O_4$	286.7	50.27	5.27	9.77	50.41	5.38	9.6
3c	Br^-	1	95	CH_3CN	167–169	$C_{14}H_{19}BrN_2$	295.2	56.94	6.44	9.49	56.61	6.52	9.2
3d	Br^-	12[b])	70	EtOH/Et_2O	177–179	$C_9H_{10}BrN$	212.1	50.37	4.75	6.60	50.73	4.73	6.4
3e	ClO_4^-	1	48	EtOH/H_2O	126–132	$C_{14}H_{12}ClNO_4 + ½ H_2O$	302.7	55.55	4.32	4.63	55.25	3.98	4.4

[a]) Yield of crude chloride. Characterized as ClO_4^- salt.
[b]) Yield after 1 h: 40%.

Procedures for the Synthesis of Pyridinio Halides **4**. – *Method A.* A mixture of **2a** (0.7 g, 10 mmol), **1** (10 mmol) and **1** · HCl (10 mmol) in CH_3CN (20 ml) was refluxed for the time indicated in *Table 4*. After cooling, the precipitated crystals were filtered off and converted into the perchlorate for recrystallization.

Method B. A mixture of **3** or **5** (5 mmol), free base **1** (5 mmol) and **1** · HCl (5 mmol) in EtOH (10 ml) was refluxed for 3 h. After removal of the solvent, the remaining solid was washed carefully with acetone. The hygroscopic **4** · halides were transformed into the perchlorates before recrystallization.

Method C. A mixture of **1e** (1.55 g, 10 mmol) and **2b** (1.61 g, 10 mmol) in EtOH (20 ml) was refluxed for 30 min. The precipitated solid was filtered off, washed with Et_2O and recrystallized. Additional preparative and analytical information is contained in *Table 3*.

Procedures for the Rearrangement of **3** *into 4-Substituted 1-Propadienylpyridinium Salts* **5**. – *Method A.* A solution of **3** (10 mmol) in EtOH (10 ml) was stirred at r.t. for 2.5 h in the presence of Et_3N (1.1 ml, 8 mmol). The solvent was removed and the remaining residue washed with Et_2O and converted to the perchlorate (except **5c**) for further purification.

Method B. A solution of **3** (5 mmol) in $CHCl_3$ (40 ml) or CH_2Cl_2/EtOH (1:1, 40 ml) was stirred at r.t. in the presence of anh. K_2CO_3 (2.7 g, 20 mmol) for 2 h. The inorganic salt was filtered off. Workup as in *Method A* gave **5**. For additional preparative information and analyses see *Table 4*.

Procedures for the Conversion of **3** *or* **5** *into 4-Substituted 1-Acetonylpyridinium Salts* **8**. – *Method A.* A solution of **3** or **5** (5 mmol) in CH_3CN (25 ml) or EtOH (20 ml) was refluxed with Et_2NH (0.44 g, 6 mmol) for 3 h. After removal of the solvent, the brownish oily residue was crystallized by stirring with Et_2O. The solid was collected and converted into the perchlorate for recrystallization *(Table 5)*.

Method B. Compounds **9a** or **9b** (5 mmol) were dissolved in HCl (20 ml, 1M) and stirred for 2 h at r.t. After concentration of the solution, the pyridinium halides **8a** and **8b** were precipitated by addition of Et_2O, filtered and converted into the perchlorates for recrystallization. For additional preparative information and analyses see *Table 5*.

Table 3. *Preparative and Analytical Data for Salts* **4**

Compound	Anion	Method[a])	Time [h]	Yield [%]	Recrystallization solvent	M.p. [°C]	Formula	M.W.	Calc. [%]			Found [%]		
									C	H	N	C	H	N
4a	ClO_4^-	B	3	58	EtOH	236–238	$C_{17}H_{24}Cl_2N_4O_8$	483.3	42.25	5.01	11.59	42.14	4.84	11.26
4b	ClO_4^-	B	3	78	CH_3CN	244–245	$C_{21}H_{28}Cl_2N_4O_8$	535.2	47.12	5.26	10.46	47.32	5.29	10.58
4d	ClO_4^-	A	23	64[b])	EtOH/H_2O	290–292	$C_{15}H_{18}Cl_2N_2O_8$	425.2	42.37	4.27	6.59	42.47	4.41	6.49
4e	Br^-	C	0.5	90	EtOH/CH_3CN	271–273	$C_{25}H_{22}Br_2N_2$	510.3	58.85	4.34	5.49	58.58	4.31	5.13
4f	ClO_4^-	A	19	52[b])	EtOH/H_2O	271–273	$C_{13}H_{14}Cl_2N_2O_8$	397.2	39.31	3.55	7.06	39.25	3.54	6.87

[a]) For *Methods A, B* and *C* see *Exper. Part.*
[b]) Yield of crude chloride, characterized as the ClO_4^- salt.

Table 4. *Preparative and Analytical Data for 1-Propadienylpyridinium Salts* **5**

Compound	Anion	Method[a])	Yield [%]	Recrystallization solvent	M.p. [°C]	Formula	M.W.	Calc. [%]			Found [%]		
								C	H	N	C	H	N
5a	ClO_4^-	A/B	96	EtOH	141–143	$C_{10}H_{13}ClN_2O_4$	260.7	46.07	5.02	10.75	46.09	5.31	10.66
5b	ClO_4^-	A/B	95	EtOH	124–125	$C_{12}H_{15}ClN_2O_4$	286.7	50.27	5.27	9.77	50.23	5.14	9.50
5c	Br^-	A/B	95	EtOH	157–160	$C_{14}H_{19}BrN_2$	295.2	56.94	6.44	9.49	57.06	6.64	9.70
5d	ClO_4^-	B	95	EtOH	67–70	$C_9H_{10}ClNO_4$	231.6	46.67	4.35	6.05	46.29	4.57	6.03
5e	ClO_4^-	B	95	EtOH	155–162	$C_{14}H_{12}ClNO_4$	293.7	57.25	4.12	4.77	56.91	3.92	4.77

[a]) For *Methods A* and *B* see *Exper. Part.*

Table 5. *Preparative and Physical Data for 1-Acetonylpyridinium Perchlorates* **8**

Compound	Method[a])	Yield [%]	Recrystallization solvent	M.p. [°C]	Formula	M.W.	Calc. [%]			Found [%]		
							C	H	N	C	H	N
8a	A	75	EtOH/	154–156	$C_{10}H_{15}ClN_2O_5$	278.7	43.09	5.43	10.05	43.44	5.74	10.04
	B	95	Et_2CO									
8b	A	90	EtOH	150–152	$C_{12}H_{17}ClN_2O_5$	304.7	47.29	5.62	9.19	46.94	5.73	9.01
	B	95										
8c	A	90	EtOH	167–170	$C_{14}H_{21}ClN_2O_5$	332.7	50.53	6.36	8.42	50.89	6.56	8.35

[a]) For *Methods A* and *B* see *Exper. Part.*

General Procedure for the Synthesis of the 4-Substituted 1-(2-Methoxypropenyl)pyridinium Perchlorates **9**. Compound **3** or **5** (5 mmol) was added to a solution of CH_3ONa in CH_3OH (prepared from 5 mmol of Na in 20 ml of MeOH) and stirred for 5 h at r.t. After removal of the solvent, the remaining **9** · halides were converted into the perchlorates and recrystallized from MeOH.

1-(2-Methoxy-2-propenyl)-4-(dimethylamino)pyridinium Perchlorate (**9a**). Yield: 1.4 g (98%) **9a** · perchlorate as white prisms, m.p. 133°. ^{1}H-NMR ((D$_6$)DMSO): 3.35 (*s*, 6H, $N(CH_3)_2$); 3.60 (*s*, 3H, CH_3O); 4.40 and 4.50 (*AB*-system, J_{AB} = 2, 2H, $=CH_2$); 4.95 (*s*, 2H, CH_2); 7.20 and 8.45 (A_2X_2-system, J_{AX} = 8, 4H, aromat. H). ^{13}C-NMR ((D$_6$)DMSO): 39.7 (*q*, $N(CH_3)_2$)); 55.3 (*q*, CH_3O); 58.7 (*t*, NCH_2); 86.6 (*t*, $=CH_2$); 107.6 (*d*, pyridinium β-C); 142.0 (*d*, pyridinium α-C); 155.9 (*s*, $=COCH_3$); 156.8 (*s*, pyridinium α-C). Anal. calc. for $C_{11}H_{17}ClN_2O_5$ (302.6): C 45.14, H 5.85, N 9.57; found: C 44.84, H 5.79, N 9.45.

1-(2-Methoxy-2-propenyl)-4-(1-pyrrolidinyl)pyridinium Perchlorate (**9b**). Yield: 1.5 g (95%) **9b** · perchlorate as white prisms, m.p. 118–119°. ^{1}H-NMR ((D$_6$)DMSO): 2.10 (*m*, 4H, CH_2CH_2); 3.55 (*m*, 4H, CH_2NCH_2); 3.60 (*s*, 3H, OCH_3); 4.40 and 4.50 (*AB*-system, J_{AB} = 2, 2H, $=CH_2$); 4.95 (*s*, 2H, CH_2); 7.10 and 8.40 (A_2X_2-system, J_{AX} = 8, 4H, aromat. H). ^{13}C-NMR ((D$_6$)DMSO): 24.6 (*t*, CH_2CH_2); 48.3 (*t*, CH_2NCH_2); 55.3 (*q*, OCH_3); 58.7 (*t*, CH_2); 86.5 (*t*, $=CH_2$); 108.1 (*d*, pyridinium β-C); 141.9 (*d*, pyridinium α-C); 153.1 (*s*, $=COCH_3$); 156.8 (*s*, pyridinium γ-C). Anal. calc. for $C_{13}H_{19}ClN_2O_5$ (328.5): C 48.99, H 6.00, N 8.79; found: C 49.34, H 6.23, N 8.74.

(E)-1-(2,3-Dibromo-1-propenyl)-4-(dimethylamino)pyridinium Perchlorate (**10**). A solution of Br_2 (0.9 g, 5.6 mmol) in $CHCl_3$ (5 ml) was added dropwise to a stirred suspension of **5a** · ClO_4^- (1.3 g, 5 mmol) in $CHCl_3$ (20 ml) at r.t. The suspension was stirred until a pale yellow solution was formed. The solvent was evaporated and the remaining crystalline residue heated under reflux in EtOH (10 ml) for 30 min. Removal of the solvent and recrystallization (EtOH) furnished pure **10** · perchlorate (2.0 g, 95%) as white needles, m.p. 152–154°. ^{1}H-NMR ($CDCl_3$/CF_3COOH): 3.43 (*s*, 6H, $N(CH_3)_2$); 4.24 (*s*, 2H, CH_2); 7.36 (*s*, 1H, =CH); 7.10 and 8.05 (A_2X_2-system, J_{AX} = 8, 4H, aromat. H). ^{13}C-NMR ((D$_6$)DMSO): 23.4 (*t*, CH_2); 40.1 (*q*, $N(CH_3)_2$); 100.5 (*d*, pyridinium β-C); 116.2 (*s*, BrC=); 124.4 (*d*, NCH=); 132.4 (*d*, pyridinium α-C); 147.1 (*s*, pyridinium γ-C). Anal. calc. for $C_{10}H_{13}Br_2ClN_2O_4$ (420.4): C 28.56, H 3.12, N 6.66; found: C 28.78, H 3.17, N 6.62.

1-(2,3-Dibromo-2-propenyl)-4-(dimethylamino)pyridinium Perchlorate (**11a**). A solution of Br_2 (1.08 g, 6 mmol) in $CHCl_3$ (5 ml) was added to a suspension of **3a** (1.3 g, 5 mmol) in $CHCl_3$ (25 ml) at r.t. A clear solution was formed. Stirring was continued for 30 min. The solvent was evaporated and the crystalline residue refluxed in EtOH (30 ml) for 1 h. Removal of the solvent gave **11a** · bromide, which was recrystallized from EtOH (1.9 g, 90%), as white needles, m.p. 139–141°. ^{1}H-NMR ($CDCl_3$/CF_3COOH): 3.26 (*s*, 6H, $N(CH_3)_2$); 5.14 (*s*, 2H, CH_2); 6.94 (*s*, 1H, CHBr); 6.89 and 7.88 (A_2X_2-system, J_{AX} = 8, 4H, aromat. H). ^{13}C-NMR ($CDCl_3$/CF_3COOH): 39.7 (*q*, $N(CH_3)_2$); 60.7 (*t*, CH_2); 108.2 (*d*, pyridinium β-C); 110.7 (*d*, =CHBr); 116.8 (*s*, =CBr); 141.5 (*d*, pyridinium α-C); 157.1 (*s*, pyridinium γ-C). Anal. calc. for $C_{10}H_{13}Br_3N_2$ (400.9): C 29.95, H 3.27, N 6.99; found: C 29.96, H 3.24, N 6.85.

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